

PATENT ABSTRACTS OF JAPAN

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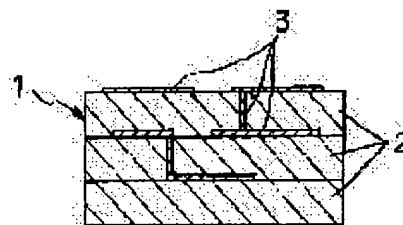
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(54) ALUMINUM NITRIDE SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the formation of pinholes and improve the reliability of a plated layer in the case of forming a thin metallized layer or plated layer on the surface of a sintered aluminum nitride.

SOLUTION: This aluminum nitride substrate 1 is produced by applying a metallized layer 3 on the surface of an insulating substrate 2 made of a sintered aluminum nitride composed mainly of aluminum nitride. The total amount of sulfur and calcium in the sintered aluminum nitride 2 is controlled to ≤ 250 ppm.



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OPERATION

[Function] nature sintering of alumimium nitride which forms an insulating base in the nature substrate of alumimium nitride possessing a metallized layer according to this invention -- a deposit of the compound of sulfur and calcium can be suppressed by setting the amount of sulfur and the amount of calcium in the inside of the body to 250 ppm or less by ****

[0012] In the nature sintered compact of alumimium nitride, sulfur and calcium are unescapable elements and cannot recognize existence of these elements that there is nothing. It is important for a deposit of the compound of sulfur and calcium to be unable to cancel, even if it reduces either calcium or sulfur, but to reduce the both sides of calcium and sulfur. The amount of sulfur and the amount of calcium are 250 ppm or less especially, and it is desirable especially to reduce the amount of sulfur to 60 ppm or less, and to reduce the amount of calcium to 180 ppm or less.

[0013] Moreover, sulfur and calcium can control the amount of sulfur and the amount of calcium in a sintered compact by using the alumimium nitride raw material powder of a high grade with which sulfur and the amount of calcium were reduced as alumimium nitride raw material powder, in order for the most to mix as an unescapable component of alumimium nitride raw material powder and to reduce these amounts.

[0014] Thereby, as a result of suppressing formation of the pinhole of a metallized layer and a deposit, when the thickness of a metallized layer is thin, a reliable wiring layer can be formed.

[0015]

[Embodiments of the Invention] The nature substrate 1 of alumimium nitride of this invention possesses the insulating base 2 which consists of a nature sintered compact of alumimium nitride, and the metallized layer 3 formed in the front face and the interior of a substrate 1, as shown in drawing 1. Moreover, a deposit may be further formed in the front face of a metallized layer 3.

[0016] The nature sintered compact of alumimium nitride used as an insulating base in this invention The material of the common knowledge as a sintering acid to alumimium nitride raw material powder the [for example, /, such as Y, Er Yb, Ho, Lu, La, and Dy, / periodic-table] -- the oxide of 3a group element -- A fluoride, carbide, a boride, a nitride, and the oxide of an alkaline-earth element, The forming means of a request of what added a fluoride, carbide, the boride, the nitride, etc. at 0.1 - 20% of the weight of a rate, For example, it is the high-density sintered compact of 98% or more of relative density obtained by calcinating in 1600-2000-degree C nitrogen content atmosphere after fabricating in arbitrary configurations by the die press, the cold isostatic press, extrusion molding, etc. In addition, addition content of periodic-table the 4a, such as Ti, Nb, V, Ta, W, Mo, Co, nickel, and Fe, 5a and 6a, the oxide carbide of 8 group element, the nitride, etc. can also be carried out at 10 or less % of the weight of a rate as for example, a coloring component as addition components other than a sintering acid at this sintered compact.

[0017] When adding such an addition component, naturally it is necessary to control to satisfy the range which mixing of the sulfur from these addition components and calcium mentioned above as the whole sintered compact.

[0018] according to this invention -- this nature sintering of alumimium nitride -- it is important that 250

ppm or less of contents of the sulfur in the inside of the body and calcium are 200 ppm or less and especially 150 ppm or less in ****. If sulfur and the amount of calcium exceed 250 ppm by ****, this is sintering process, the compound of the shape of a sunspot which makes calcium and sulfur a subject on the surface of a sintered compact will deposit, and the problem that a pinhole will be formed at the time of formation of a metallized layer will produce it.

[0019] Desirably, it is good that sulfur is 60 ppm or less and calcium is 180 ppm or less.

[0020] Sulfur is mixed mainly from aluminum nitride raw material powder. The sulfur component in the carbon added as a reducing agent at the time of this sulfur producing aluminum nitride powder for example, by alumina reduction nitriding is considered to have remained in raw material powder. Moreover, it is the component which also mixes calcium as an unescapable impurity, and reduction of sulfur and the amount of calcium can be aimed at by using carbon with few amounts of sulfur at the time of composition of aluminum nitride raw material powder, or performing high grade-ized processing by refining processing of raw material powder.

[0021] Moreover, it is required to use the powder of a high grade so that the range of the above [the sulfur and the amount of calcium of the whole sintered compact] can be satisfied also in the addition component of the sintering acid and others which are added to aluminum nitride raw material powder and which were mentioned above.

[0022] In this invention, in order to produce the substrate which has a metallized layer, a sheet-like Plastic solid is produced using the mixture which blended with aluminum nitride raw material powder an addition component of a sintering acid or others which was mentioned above. A sheet-like Plastic solid can prepare the slurry which consists of the above-mentioned mixture, and can produce it by the doctor blade method, or can be produced by press forming, extrusion molding, etc.

[0023] Next, a metallizing paste is applied to the obtained sheet-like Plastic solid (green sheet). a metallizing paste is main in at least one sort of refractory metals chosen from W, Mo, and Ta -- carrying out -- a case -- the [, such as rare earth elements and an actinoids, / periodic-table] -- the [, such as 3a group element, and Ti, Zr, / periodic-table] -- 4a group element can be contained and addition content of the aluminum nitride which is the component which forms an insulating base, and the sintering-acid component can be carried out further

[0024] After the through hole which was printed on the surface of the green sheet, or was formed in the green sheet by screen printing etc. is filled up, simultaneous baking of this metallizing paste is carried out with a green sheet. Especially simultaneous baking is calcinated in nitrogen hydrogen mixture atmosphere among 1600-2000-degree C nitrogen atmosphere.

[0025] Although the thickness of the metallized layer formed as mentioned above is generally about 15-25 micrometers according to this invention, even if thickness is the thin metallized layer which is 5-15 micrometers, a highly reliable METALIZU layer can be formed as a wiring layer according to the effect which suppressed formation of a pinhole like this invention.

[0026] Thus, covering formation of the deposits, such as nickel and Au, can be further carried out by the thickness of 3-8 micrometers by electrolysis plating or the electroless deposition method at the obtained substrate for the purpose of carrying out low attachment of the metallic ornaments, such as a lead pin.

[0027] Hereafter, the following example explains this invention.

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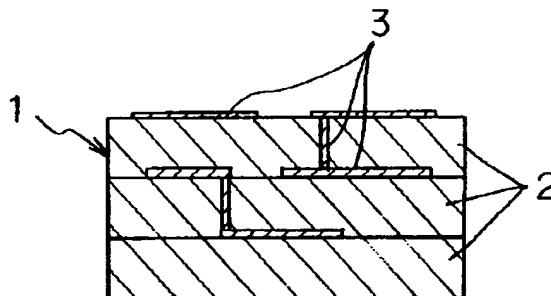
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(54) 【発明の名称】 窒化アルミニウム質基板

(57) 【要約】

【課題】 窒化アルミニウム質焼結体の表面に薄層のメタライズ層やメッキ層を形成した時、ピンホールが形成され、メタライズ層の信頼性を損ねていた。

【解決手段】 窒化アルミニウムを主成分とする窒化アルミニウム質焼結体からなる絶縁基体2の表面にメタライズ層3を配設してなる窒化アルミニウム質基板1において、窒化アルミニウム質焼結体2中におけるイオウおよびカルシウムの含有量を含量で250ppm以下に制御する。



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【特許請求の範囲】

【請求項1】窒化アルミニウムを主成分とする窒化アルミニウム質焼結体からなる絶縁基板の少なくとも表面にメタライズ層を配設してなる窒化アルミニウム質基板において、前記窒化アルミニウム質焼結体中におけるイオウおよびカルシウムの含有量が含量で250ppm以下であることを特徴とする窒化アルミニウム質基板。

【請求項2】前記窒化アルミニウム質焼結体中におけるイオウ含有量が60ppm以下、カルシウム含有量が180ppm以下である請求項1記載の窒化アルミニウム質基板。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、配線基板などに好適に使用されるメタライズ層が形成された窒化アルミニウム質基板に関するものである。

【0002】

【従来技術】従来より、窒化アルミニウム質焼結体は、アルミナ、ジルコニアなどのセラミック材料に比較して格段に熱伝導性に優れたセラミック材料として注目され、半導体素子からの発熱を効率的に除去するために、配線基板や半導体素子収納用パッケージにおける基板材料として用いられつつある。

【0003】このような窒化アルミニウム質焼結体としては、窒化アルミニウムがそれ自体では焼結しにくいために、 Y_2O_3 などの周期律表第3a族元素化合物、 CaO などのアルカリ土類金属元素化合物などを添加し焼成することが、特開昭60-71575号、特公昭58-49510号、特開昭61-117160号等にて提案されている。

【0004】また、窒化アルミニウム質焼結体に添加される上記焼結助剤成分は、最終焼結体中に残存すると熱伝導性を低下させる要因となるため、高熱伝導化を達成するために、これら助剤成分を揮散除去させた高純度窒化アルミニウム焼結体も特開昭62-41767号、特開昭63-277569号等にて提案されている。

【0005】さらに、窒化アルミニウム質焼結体を用いて配線基板等を作製するには、例えば、窒化アルミニウム質グリーンシートの表面にW、Moなどの高融点金属を含有するペーストを配線パターンに塗布した後、これを1600~1900℃の温度でメタライズ層と絶縁基板とを同時焼成することにより作製することが知られている。また、基板の表面に形成されたメタライズ層の表面には、リードピンなどの金具をロウ付けするために、NiやAuなどのメッキが被覆されている。

【0006】

【発明が解決しようとする課題】配線基板は、その高密度化および小型化に伴い、メタライズ層も薄膜化する傾向にある。そこで、高密度の配線基板等を作製するに、窒化アルミニウム質グリーンシートにメタライズベース

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トを塗布し、これを同時焼成したところ、メタライズ層にピンホールが形成されるといった問題があった。

【0007】このようなピンホールの形成は、配線の薄膜化および高密度化に対しては回路としての信頼性を損なうため、致命的な問題であった。しかも、メタライズ層の表面にさらにメッキ層を形成した場合、ピンホールの箇所ではメッキ層が形成されないという問題があった。

【0008】

【課題を解決するための手段】本発明者は、かかる現象について研究を進めた結果、ピンホールの形成箇所には、窒化アルミニウム質焼結体の表面に黒色状の析出物が存在すること、しかもその析出物がカルシウムとイオウとを主体とする化合物からなること、その析出物がメタライズとの濡れ性が極端に悪いためにピンホールが形成され、その結果、その箇所にメッキが形成されないことを突き止めた。

【0009】そこで、本発明者は、メタライズ層を形成する窒化アルミニウム質焼結体中において、イオウ(S)およびカルシウム(Ca)の量の含有量の少ない窒化アルミニウム原料粉末を用いて焼結し、最終焼結体中におけるイオウ量およびカルシウム量を特定範囲に低減した焼結体を用いた結果、黒点状の析出物がなくなり、メタライズ層およびメッキ層においてピンホールの形成を抑制できることを見だし、本発明に至ったのである。

【0010】即ち、本発明は、窒化アルミニウムを主体とする窒化アルミニウム質焼結体からなる基板の少なくとも表面にメタライズ層を具備してなる窒化アルミニウム質基板において、前記窒化アルミニウム質焼結体中におけるイオウおよびカルシウムの含有量が含量で250ppm以下であることを特徴とするものである。

【0011】

【作用】本発明によれば、メタライズ層を具備する窒化アルミニウム質基板において、絶縁基板を形成する窒化アルミニウム質焼結体中におけるイオウ量およびカルシウム量を含量で250ppm以下とすることにより、イオウおよびカルシウムの化合物の析出を抑制することができる。

【0012】イオウおよびカルシウムは、窒化アルミニウム質焼結体においては、不可避的な元素であり、これらの元素の存在を皆無にすることはできない。イオウとカルシウムとの化合物の析出は、カルシウムまたはイオウのいずれか一方を低減しても解消することができず、カルシウムとイオウの双方を低減することが重要である。特に、イオウ量とカルシウム量が250ppm以下で、特にイオウ量を60ppm以下、カルシウム量を180ppm以下に低減することが望ましい。

【0013】また、イオウおよびカルシウムは、そのほとんどが窒化アルミニウム原料粉末の不可避的な成分として混入するものであり、これらの量を低減するには、

窒化アルミニウム原料粉末として、イオウおよびカルシウム量が低減された高純度の窒化アルミニウム原料粉末を用いることにより、焼結体中のイオウ量およびカルシウム量を制御することができる。

【0014】これにより、メタライズ層およびメッキ層のピンホール形成が抑制される結果、メタライズ層の厚みが薄い場合においても信頼性の高い配線層を形成することができる。

【0015】

【発明の実施の形態】本発明の窒化アルミニウム質基板1は、図1に示すように、窒化アルミニウム質焼結体からなる絶縁基体2と、基板1の表面および内部に形成されたメタライズ層3を具備する。また、メタライズ層3の表面には、さらにメッキ層が形成される場合もある。

【0016】本発明において絶縁基体として用いられる窒化アルミニウム質焼結体は、窒化アルミニウム原料粉末に、焼結助剤として周知の材料、例えば、Y、Er、Yb、Ho、Lu、La、Dyなど周期律表第3a族元素の酸化物、フッ化物、炭化物、硼化物、窒化物や、アルカリ土類元素の酸化物、フッ化物、炭化物、硼化物、窒化物等を0.1~20重量%の割合で添加したものを所望の成形手段、例えば、金型プレス、冷間静水圧プレス、押出し成形等により任意の形状に成形後、1600~2000℃の窒素含有雰囲気中で焼成することにより得られた相対密度98%以上の高密度焼結体である。なお、かかる焼結体には、焼結助剤以外の添加成分として、例えば、着色成分として、Ti、Nb、V、Ta、W、Mo、Co、Ni、Feなどの周期律表第4a、5a、6a、8族元素の酸化物炭化物、窒化物などを10重量%以下の割合で添加含有することもできる。

【0017】このような添加成分を添加する場合においても、これらの添加成分からのイオウおよびカルシウムの混入が焼結体全体として前述した範囲を満足するように制御する必要があることは当然である。

【0018】本発明によれば、この窒化アルミニウム質焼結体中におけるイオウおよびカルシウムの含有量が含量で250ppm以下、特に200ppm以下、さらには150ppm以下であることが重要である。これは、イオウおよびカルシウム量が含量で250ppmを越えると、焼結過程で、焼結体の表面にカルシウムとイオウを主体とする黒点状の化合物が析出しメタライズ層の形成時にピンホールが形成されてしまうという問題が生じる。

【0019】望ましくは、イオウは、60ppm以下、カルシウムは180ppm以下であるのがよい。

【0020】イオウは、主として窒化アルミニウム原料粉末から混入する。このイオウは、例えば、アルミナ還元窒化法によって窒化アルミニウム粉末を作製する際の還元剤として添加されたカーボン中のイオウ成分が原料粉末中に残存したものと考えられる。また、カルシウム

も不可避的不純物として混入する成分であり、窒化アルミニウム原料粉末の合成時にイオウ量の少ないカーボンを用いるか、あるいは原料粉末の精製処理により高純度化処理を行うことによりイオウおよびカルシウム量の低減を図ることができる。

【0021】また、窒化アルミニウム原料粉末に対して添加される上述した焼結助剤およびその他の添加成分においても焼結体全体のイオウおよびカルシウム量が上記の範囲を満足できるように高純度の粉末を用いることが必要である。

【0022】本発明において、メタライズ層を有する基板を作製するには、窒化アルミニウム原料粉末に、上述したような焼結助剤やその他の添加成分を配合した混合物を用いて、シート状成形体を作製する。シート状成形体は、上記混合物からなるスラリーを調製してドクターブレード法により作製するか、またはプレス成形、押出し成形等によっても作製することができる。

【0023】次に、得られたシート状成形体（グリーンシート）に対して、メタライズペーストを塗布する。メタライズペーストは、W、MoおよびTaから選ばれる少なくとも1種の高融点金属を主とし、場合によっては、希土類元素、アクチノイド元素などの周期律表第3a族元素や、Ti、Zrなどの周期律表第4a族元素を含有するものであり、さらに、絶縁基体を形成する成分である窒化アルミニウムや、焼結助剤成分を添加含有させることもできる。

【0024】このメタライズペーストは、スクリーン印刷法等により、グリーンシートの表面に印刷され、あるいはグリーンシートに形成されたスルーホールに充填された後に、グリーンシートとともに同時焼成される。同時焼成は、1600~2000℃の窒素雰囲気中、特に窒素水素混合雰囲気中で焼成される。

【0025】本発明によれば、上記のようにして形成されるメタライズ層の厚みは一般には15~25μm程度であるが、本発明のようにピンホール形成を抑制した効果によって、厚みが5~15μmの薄いメタライズ層であっても配線層として高信頼性のメタライズ層を形成することができる。

【0026】このようにして、得られた基板には、さらに、リードピン等の金具をロウ付けすることを目的として、電解メッキ、または無電解メッキ法によりNi、Auなどのメッキ層を3~8μmの厚みで被覆形成することができる。

【0027】以下、本発明を次の例で説明する。

【0028】

【実施例】窒化アルミニウム原料粉末として、アルミナ還元窒化法により得られた表1に示す5種類の原料を用意した。

【0029】

【表1】

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	平均粒径 (μm)	酸素量 (重量%)	S 量 (ppm)	Ca 量 (ppm)	他の陽イオン 不純物 (ppm)
原料A	1.30	0.85	30	50	90
原料B	1.46	0.85	40	70	61
原料C	1.50	0.82	55	80	62
原料D	1.49	0.80	65	120	65
原料E	1.43	0.84	110	140	61
原料F	1.57	0.85	135	170	75
原料G	1.55	0.83	130	210	89

【0030】上記表1の原料に対して、 Er_2O_3 あるいは Y_2O_3 を表2に示す割合で添加混合したものに、さらにバインダーとしてアクリル系バインダーを添加して窒化ケイ素ボールを用いたボールミルで40時間混合してスラリーを調製した。このスラリーを用いてドクターブレード法により厚み0.5mmのグリーンシートを作製した。その後、このグリーンシートの表面に、固形成分として、W94.5重量%、AlN5重量%、 Er_2O_3 0.5重量%含有し、これをジブチルフタレート

からなる溶媒中に分散したメタライズペーストを回路パターンの代わりに、ピンホールを検出するために10mm角に印刷した。

【0031】そして、これを1000℃で脱バインダー処理し、 $\text{N}_2/\text{H}_2=82:18$ の窒素水素混合雰囲気中で10時間同時焼成し、メタライズ層の厚みが10μmの窒化アルミニウム質基板を作製した。

【0032】得られた基板の窒化アルミニウム質焼結体*

試料 No.	AlN 原料の 種類	助剤量	S 量 (ppm)	Ca 量 (ppm)	S + Ca 合計量 (ppm)	ピンホールの 数 (個)	接合強度 (kgf)	熱伝導率 (W/mk)
1	原料A	Er_2O_3 6	18	48	66	0	4.5	152
2	原料B	Er_2O_3 6	25	72	97	0	4.7	158
3	原料C	Er_2O_3 6	34	76	110	0	4.0	155
4	原料D	Er_2O_3 6	42	115	157	15	3.5	157
5	原料E	Er_2O_3 6	73	135	208	25	3.3	155
* 6	原料F	Er_2O_3 6	90	170	260	110	0.2	150
* 7	原料G	Er_2O_3 6	82	200	282	135	0.1	151
8	原料B	Y_2O_3 6	28	60	88	0	4.5	160
* 9	原料F	Y_2O_3 6	85	170	255	120	0.2	165
10	原料A	Er_2O_3 8	20	44	64	0	4.4	155
11	原料D	Y_2O_3 8	45	110	155	10	3.4	155

*印は本発明の範囲外の試料を示す。

【0036】表2の結果から明らかなように、焼結体中のイオウおよびカルシウムの含有量が合計で250ppmを越える試料No. 6, 7, 9はいずれも、焼結体の表面に黒点状の析出物が認められ、メタライズ層にピンホールが数多く認められた。この析出物をEPMA (マイ

*に対して、ICP発光分光分析によって、焼結体中のイオウおよびカルシウム量を定量し表2に示した。また、窒化アルミニウム質焼結体のレーザーフラッシュ法により測定した熱伝導率も合わせて表2に示した。

【0033】また、得られた基板のメタライズ層に対して、双眼顕微鏡によって、10mm角のメタライズ層中のピンホールの数をカウントしてその数を表2に示した。

【0034】さらに、メタライズ層の基板への密着性を調査するために、メタライズ層に対して、無電解メッキ法によってNiメッキを4μm形成した後、Fe-Ni-Co合金からなるピンをBAg-8によってロウ付けした後、リードピンを垂直に引っ張ることによりメタライズ層の接合強度を測定した。その結果を表2に示す。

【0035】

【表2】

※クロアナライザー)で分析した結果、イオウとカルシウムが検出された。

【0037】これに対して、イオウとカルシウムの合計量が250ppm以下の本発明品はいずれもピンホールの数が格段に減少し、特にSとCaの合計が200ppm

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m以下で20個以下、150ppm以下でほとんど皆無となった。また、メタライズ層の接合強度も高く、熱伝導度も高いものであった。

【0038】

【発明の効果】以上詳述した通り、本発明の窒化アルミニウム質基板によれば、黒点状の析出物によるメタライズ層およびメッキ層へのピンホール形成を抑制することができるためにメタライズ層からなる配線層の信頼性を高めるとともに、メタライズ層の薄層化および高密度

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化を可能とすることができる。

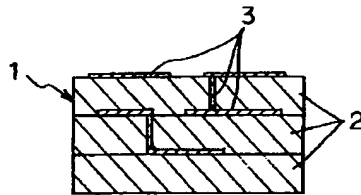
【図面の簡単な説明】

【図1】本発明の窒化アルミニウム質基板の構造を示す図である。

【符号の説明】

- 1 窒化アルミニウム質基板
- 2 窒化アルミニウム質焼結体
- 3 メタライズ層

【図1】



* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nature substrate of alumimium nitride in which the metallized layer used suitable for a wiring substrate etc. was formed.

[0002]

[Description of the Prior Art] conventionally, the nature sintered compact of alumimium nitride is used as a substrate material in a wiring substrate or the package for semiconductor device receipt, in order to be observed as a ceramic material which was markedly alike as compared with ceramic material, such as an alumina and a zirconia, and was excellent in thermal conductivity and to remove generation of heat from a semiconductor device efficiently

[0003] since it is hard to sinter alumimium nitride as such a nature sintered compact of alumimium nitride in itself -- Y₂O₃ etc. -- the [periodic-table] -- adding and calcinating alkaline-earth-metal element compounds, such as 3a group element compound and CaO, etc. is proposed in JP,60-71575,A, JP,58-49510,B, JP,61-117160,A, etc.

[0004] moreover, the above-mentioned sintering-acid component added by the nature sintered compact of alumimium nitride -- the last sintering -- since it will become the factor which reduces thermal conductivity if it remains inside of the body, in order to attain high temperature conduction-ization, the high grade alumimium nitride sintered compact which carried out vaporization removal of these assistant component is also proposed in JP,62-41767,A, JP,63-277569,A, etc.

[0005] Furthermore, after applying to a circuit pattern the paste which contains refractory metals, such as W and Mo, on the front face of the nature green sheet of alumimium nitride in order to produce a wiring substrate etc. using the nature sintered compact of alumimium nitride for example, producing this by carrying out simultaneous baking of a metallized layer and the insulating substrate at the temperature of 1600-1900 degrees C is known. Moreover, in order to carry out low attachment of the metallic ornaments, such as a lead pin, plating of nickel, Au, etc. is covered by the front face of the metallized layer formed on the surface of the substrate.

[0006]

[Problem(s) to be Solved by the Invention] A wiring substrate is in the inclination which also thin-film-izes a metallized layer with the densification and miniaturization. Then, when the metallizing paste was applied to the nature green sheet of alumimium nitride and simultaneous baking of this was carried out, the problem that a pinhole was formed in a metallized layer was to produce a high-density wiring substrate etc.

[0007] Formation of such a pinhole was a fatal problem in order to spoil the reliability as a circuit to thin-film-izing and densification of wiring. And when a deposit was further formed on the surface of a metallized layer, there was a problem that a deposit was not formed in the part of a pinhole.

[0008]

[Means for Solving the Problem] this invention person traced that a pinhole is formed in it with a bird clapper from that a black-like sludge exists in the front face of the nature sintered compact of



aluminum nitride, and the compound with which the sludge moreover makes calcium and sulfur a subject since the sludge of wettability with metallizing is extremely bad in the formation part of a pinhole, consequently plating was not formed in the part, as a result of advancing research about this phenomenon.

[0009] In the inside of the body then, nature sintering of aluminum nitride whose this invention person forms a metallized layer -- It sinters using sulfur (S) and aluminum nitride raw material powder with few contents of the amount of calcium (calcium). As a result of using the sintered compact which reduced the amount of sulfur and the amount of calcium in the last sintered compact in the specific range, the sunspot-like sludge was lost, and it found out that formation of a pinhole could be suppressed in a metallized layer and a deposit, and resulted in this invention.

[0010] namely, the nature substrate of aluminum nitride of the substrate which this invention becomes from the nature sintered compact of aluminum nitride which makes aluminum nitride a subject which comes to provide a metallized layer on a front face at least -- setting -- the aforementioned nature sintering of aluminum nitride -- it is characterized by the content of the sulfur in the inside of the body and calcium being 250 ppm or less in ****

[0011]

[Function] nature sintering of aluminum nitride which forms an insulating base in the nature substrate of aluminum nitride possessing a metallized layer according to this invention -- a deposit of the compound of sulfur and calcium can be suppressed by setting the amount of sulfur and the amount of calcium in the inside of the body to 250 ppm or less by ****

[0012] In the nature sintered compact of aluminum nitride, sulfur and calcium are unescapable elements and cannot recognize existence of these elements that there is nothing. It is important for a deposit of the compound of sulfur and calcium to be unable to cancel, even if it reduces either calcium or sulfur, but to reduce the both sides of calcium and sulfur. The amount of sulfur and the amount of calcium are 250 ppm or less especially, and it is desirable especially to reduce the amount of sulfur to 60 ppm or less, and to reduce the amount of calcium to 180 ppm or less.

[0013] Moreover, sulfur and calcium can control the amount of sulfur and the amount of calcium in a sintered compact by using the aluminum nitride raw material powder of a high grade with which sulfur and the amount of calcium were reduced as aluminum nitride raw material powder, in order for the most to mix as an unescapable component of aluminum nitride raw material powder and to reduce these amounts.

[0014] Thereby, as a result of suppressing formation of the pinhole of a metallized layer and a deposit, when the thickness of a metallized layer is thin, a reliable wiring layer can be formed.

[0015]

[Embodiments of the Invention] The nature substrate 1 of aluminum nitride of this invention possesses the insulating base 2 which consists of a nature sintered compact of aluminum nitride, and the metallized layer 3 formed in the front face and the interior of a substrate 1, as shown in drawing 1. Moreover, a deposit may be further formed in the front face of a metallized layer 3.

[0016] The nature sintered compact of aluminum nitride used as an insulating base in this invention The material of the common knowledge as a sintering acid to aluminum nitride raw material powder the [for example, /, such as Y, Er Yb, Ho, Lu, La, and Dy, / periodic-table] -- the oxide of 3a group element -- A fluoride, carbide, a boride, a nitride, and the oxide of an alkaline-earth element, The forming means of a request of what added a fluoride, carbide, the boride, the nitride, etc. at 0.1 - 20% of the weight of a rate, For example, it is the high-density sintered compact of 98% or more of relative density obtained by calcinating in 1600-2000-degree C nitrogen content atmosphere after fabricating in arbitrary configurations by the die press, the cold isostatic press, extrusion molding, etc. In addition, addition content of periodic-table the 4a, such as Ti, Nb, V, Ta, W, Mo, Co, nickel, and Fe, 5a and 6a, the oxide carbide of 8 group element, the nitride, etc. can also be carried out at 10 or less % of the weight of a rate as for example, a coloring component as addition components other than a sintering acid at this sintered compact.

[0017] When adding such an addition component, naturally it is necessary to control to satisfy the range

which mixing of the sulfur from these addition components and calcium mentioned above as the whole sintered compact.

[0018] according to this invention -- this nature sintering of alumimium nitride -- it is important that 250 ppm or less of contents of the sulfur in the inside of the body and calcium are 200 ppm or less and especially 150 more ppm or less in **** If sulfur and the amount of calcium exceed 250 ppm by ****, this is sintering process, the compound of the shape of a sunspot which makes calcium and sulfur a subject on the surface of a sintered compact will deposit, and the problem that a pinhole will be formed at the time of formation of a metallized layer will produce it.

[0019] Desirably, it is good that sulfur is 60 ppm or less and calcium is 180 ppm or less.

[0020] Sulfur is mixed mainly from alumimium nitride raw material powder. The sulfur component in the carbon added as a reducing agent at the time of this sulfur producing alumimium nitride powder for example, by alumina reduction nitriding is considered to have remained in raw material powder. Moreover, it is the component which also mixes calcium as an unescapable impurity, and reduction of sulfur and the amount of calcium can be aimed at by using carbon with few amounts of sulfur at the time of composition of alumimium nitride raw material powder, or performing high grade-ized processing by refining processing of raw material powder.

[0021] Moreover, it is required to use the powder of a high grade so that the range of the above [the sulfur and the amount of calcium of the whole sintered compact] can be satisfied also in the addition component of the sintering acid and others which are added to alumimium nitride raw material powder and which were mentioned above.

[0022] In this invention, in order to produce the substrate which has a metallized layer, a sheet-like Plastic solid is produced using the mixture which blended with alumimium nitride raw material powder an addition component of a sintering acid or others which was mentioned above. A sheet-like Plastic solid can prepare the slurry which consists of the above-mentioned mixture, and can produce it by the doctor blade method, or can be produced by press forming, extrusion molding, etc.

[0023] Next, a metallizing paste is applied to the obtained sheet-like Plastic solid (green sheet). a metallizing paste is main in at least one sort of refractory metals chosen from W, Mo, and Ta -- carrying out -- a case -- the [, such as rare earth elements and an actinoids, / periodic-table] -- the [, such as 3a group element, and Ti, Zr, / periodic-table] -- 4a group element can be contained and addition content of the alumimium nitride which is the component which forms an insulating base, and the sintering-acid component can be carried out further

[0024] After the through hole which was printed on the surface of the green sheet, or was formed in the green sheet by screen printing etc. is filled up, simultaneous baking of this metallizing paste is carried out with a green sheet. Especially simultaneous baking is calcinated in nitrogen hydrogen mixture atmosphere among 1600-2000-degree C nitrogen atmosphere.

[0025] Although the thickness of the metallized layer formed as mentioned above is generally about 15-25 micrometers according to this invention, even if thickness is the thin metallized layer which is 5-15 micrometers, a highly reliable METAIZU layer can be formed as a wiring layer according to the effect which suppressed formation of a pinhole like this invention.

[0026] Thus, covering formation of the deposits, such as nickel and Au, can be further carried out by the thickness of 3-8 micrometers by electrolysis plating or the electroless deposition method at the obtained substrate for the purpose of carrying out low attachment of the metallic ornaments, such as a lead pin.

[0027] Hereafter, the following example explains this invention.

[0028]

[Example] Five kinds of raw materials shown in Table 1 obtained by alumina reduction nitriding as alumimium nitride raw material powder were prepared.

[0029]

[Table 1]

	平均粒径 (μm)	酸素量 (重量%)	S 量 (ppm)	Ca 量 (ppm)	他の陽イオン 不純物 (ppm)
原料A	1.30	0.85	30	50	90
原料B	1.46	0.85	40	70	81
原料C	1.50	0.82	55	80	62
原料D	1.49	0.80	65	120	65
原料E	1.43	0.84	110	140	61
原料F	1.57	0.85	135	170	75
原料G	1.55	0.83	130	210	89

[0030] It is Er₂O₃ to the raw material of the above-mentioned table 1. Or Y₂O₃ To what carried out addition mixture at a rate shown in Table 2, the acrylic binder was further added as a binder, it mixed with the ball mill using the silicon nitride ball to it for 40 hours, and the slurry was prepared to it. The green sheet with a thickness of 0.5mm was produced by the doctor blade method using this slurry. Then, to the front face of this green sheet, as a formed element, it contained Er₂O₃ 0.5% of the weight, and W94.5% of the weight, 5 % of the weight of AlN(s), instead of the circuit pattern, the metallizing paste which distributed this in the solvent which consists of a dibutyl phthalate was printed on 10mm square, in order to detect a pinhole.

[0031] And ** binder processing of this was carried out at 1000 degrees C, simultaneous baking was carried out in the nitrogen hydrogen mixture atmosphere of N₂/H₂ =82:18 for 10 hours, and the nature substrate of alumimium nitride whose thickness of a metallized layer is 10 micrometers was produced.

[0032] To the nature sintered compact of alumimium nitride of the obtained substrate, with ICP emission spectral analysis, the fixed quantity of the sulfur and the amount of calcium in a sintered compact was carried out, and they were shown in Table 2. Moreover, the thermal conductivity measured with the laser flash method of the nature sintered compact of alumimium nitride was also doubled, and it was shown in Table 2.

[0033] Moreover, to the metallized layer of the obtained substrate, with the binocular microscope, the number of the pinholes in 10mm metallized layer of an angle was counted, and the number was shown in Table 2.

[0034] Furthermore, in order to investigate the adhesion to the substrate of a metallized layer, after carrying out low attachment of the pin which consists of a Fe-nickel-Co alloy after forming 4 micrometers of nickel plating by the electroless deposition method to a metallized layer by BAg-8, the bonding strength of a metallized layer was measured by pulling a lead pin perpendicularly. The result is shown in Table 2.

[0035]

[Table 2]

試料 No.	AlN 原料の 種類	助剤量	S 量 (ppm)	Ca 量 (ppm)	S + Ca 合計量 (ppm)	ピンホールの数 (個)	接合強度 (kgf)	熱伝率 (W/mk)
1	原料 A	Er ₂ O ₃ 6	18	48	66	0	4.5	152
2	原料 B	Er ₂ O ₃ 6	25	72	97	0	4.7	158
3	原料 C	Er ₂ O ₃ 6	34	76	110	0	4.0	155
4	原料 D	Er ₂ O ₃ 6	42	115	157	15	3.5	157
5	原料 E	Er ₂ O ₃ 6	73	135	208	25	3.3	155
* 6	原料 F	Er ₂ O ₃ 6	90	170	<u>260</u>	110	0.2	150
* 7	原料 G	Er ₂ O ₃ 6	82	200	<u>282</u>	135	0.1	151
8	原料 B	Y ₂ O ₃ 6	28	80	88	0	4.5	160
* 9	原料 F	Y ₂ O ₃ 6	85	170	<u>255</u>	120	0.2	165
10	原料 A	Er ₂ O ₃ 8	20	44	64	0	4.4	155
11	原料 D	Y ₂ O ₃ 8	45	110	155	10	3.4	155

* 印は本発明の範囲外の試料を示す。

[0036] The sunspot-like sludge was accepted on the surface of the sintered compact, and, as for each of sample No.6 to which the sulfur in a sintered compact and the content of calcium exceed 250 ppm in total, and 7 and 9, many pinholes were accepted in the metallized layer so that clearly from the result of Table 2. Sulfur and calcium were detected as a result of analyzing this sludge by EPMA (microanalyzer).

[0037] on the other hand, the total quantity of sulfur and calcium boiled markedly each this invention article 250 ppm or less, the number of pinholes decreased, and especially the sum total of S and calcium became that there is almost nothing by 20 or less pieces and 150 ppm or less by 200 ppm or less. Moreover, the bonding strength of a metallized layer was also high and thermal conductivity was also high.

[0038]

[Effect of the Invention] While raising the reliability of the wiring layer which consists of a metallized layer according to the nature substrate of aluminum nitride of this invention since formation of the pinhole to sunspot-like the metallized layer and deposit by the sludge can be suppressed as explained in full detail above, the lamination and densification of a metallized layer can be made possible.

[Translation done.]